

Interfacial studies of Emerging Cathode Materials

Project ID # BAT408

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2020 DOE Vehicle Technologies Office Annual Merit Review

Overview

Timeline

- Project start date 10/1/2018
- Project end date 9/30/2021
- Percent complete 60 %

Budget

- Total project funding
 - DOE share 100 %
 - Contractor share N/A
- Funding for FY2019 \$ 420 k
- Funding for FY2020 \$ 400 k

Barriers and Technical Targets

- Barriers addressed
 - Energy density
 - Cost
 - Safety

Partners

- LBNL, SSRL, ALS, VA Tech
- Project lead: LBNL

Relevance



- ❑ To reach energy density and cost goals, high capacity cathode materials with significant reversible O redox capacity should be considered. Little is currently known about the interfacial reactivity of these materials or their impact on safety and cyclability.
- ❑ We propose to investigate the interfacial properties of candidate O-redox materials using surface and bulk sensitive techniques we have developed for NMC materials in our previous projects.

Milestones-FY2019

| Milestone | Type | Date/Status |
|---|-----------|------------------|
| Complete TXM Co K-edge experiments on NMC-811 system* | Milestone | Q1/Completed |
| Select materials that undergo O redox, determine synthesis routes | Milestone | Q2/Completed |
| Synthesis candidate materials, characterize | Milestone | Q3/Completed |
| Down-select materials based on properties | Go/no go | Go decision made |

* The first part of FY2019 is devoted to finishing the prior NMC project.

Any proposed future work is subject to change based on funding levels

Milestones-FY2020

| Milestone | Type | Date/Status |
|---|-----------|--|
| Electrochemically characterize candidate materials and prepare samples for analysis | Milestone | Q1/Completed |
| Start selected synchrotron experiments (XAS,XPS,TXM,XRS) | Milestone | Q2/Underway |
| Go/no go decision on XRS | Go/no go | Q3/Stop if requirement for large sample size is an impediment or if no useful information is obtained from O k-edge data |
| Select samples for STEM/EELS analysis | Milestone | Q4/Planned |

Any proposed future work is subject to change based on funding levels

Milestones-FY2021

| Milestone | Type | Date/Status |
|--|-----------|--|
| Prepare modified candidate materials | Milestone | Q1/Planned |
| Electrochemically characterize modified candidate materials and prepare samples for analysis | Milestone | Q2/Planned |
| Go/no go decision on selected modification methods | Go/no go | Q3/Stop if selected modification methods prove ineffective |
| Perform synchrotron experiments on selected candidate materials | Milestone | Q4/Planned |

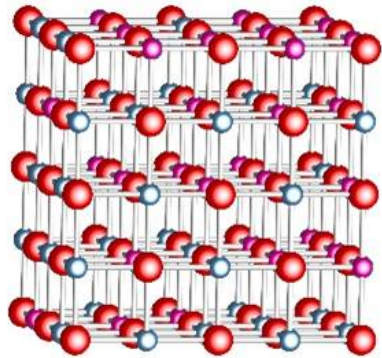
Any proposed future work is subject to change based on funding levels

Approach

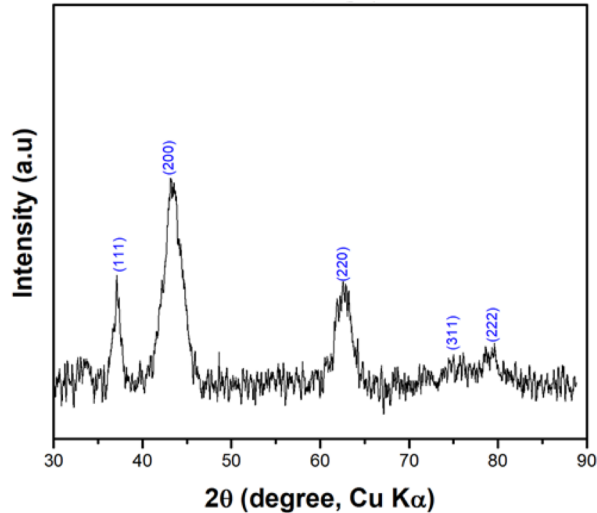
- We synthesize candidate cathode materials including NMCs (FY2018 project) and emerging cathode materials (FY2019–FY2021 project), using several different methods, and characterize them. For some experiments, we use commercial materials.
- We use an array of bulk and surface-sensitive synchrotron techniques to characterize selected cathode materials, including chemically and electrochemically delithiated samples.
- Depending on technique, information needed, and time constraints, we may perform some of these experiments *in situ* or *ex situ*.
 - *Advantage to in situ experiments is that we can capture phenomena in real time. Disadvantages are the large amount of time they take, and the possibility that the experiment design is not relevant to the device.*
 - *Advantage to ex situ experiments is that many samples can be examined in a short amount of time, and the information then used to design in situ experiments. Disadvantage is that processing samples may compromise their integrity.*
 - *In situ experiments can provide information about a system undergoing dynamic changes, while ex situ ones probe equilibrated systems. Both types of information can be relevant.*

Technical Accomplishments

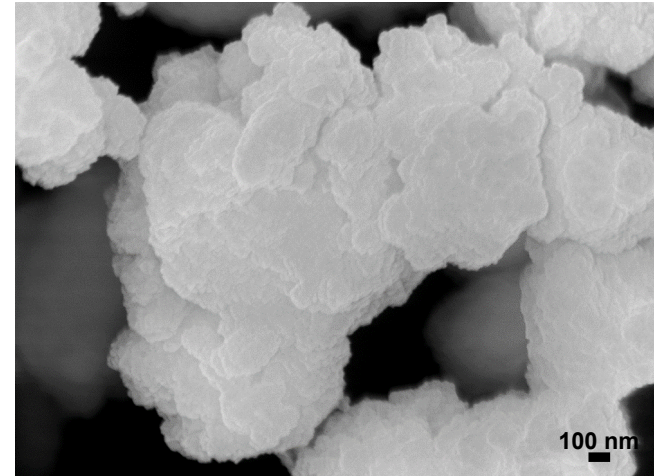
Synthesis of $\text{Li}_4\text{Mn}_2\text{O}_5$



Rock salt structure



Laboratory X-ray diffraction



SEM image

- Rock-salt type $\text{Li}_4\text{Mn}_2\text{O}_5$ was synthesized by direct mechanochemical synthesis at room temperature starting from orthorhombic LiMnO_2 and Li_2O (Pralong *et al.*, Nat. Mater. 2015, 15, 173).

Note: this data was presented last year and is provided here for context.

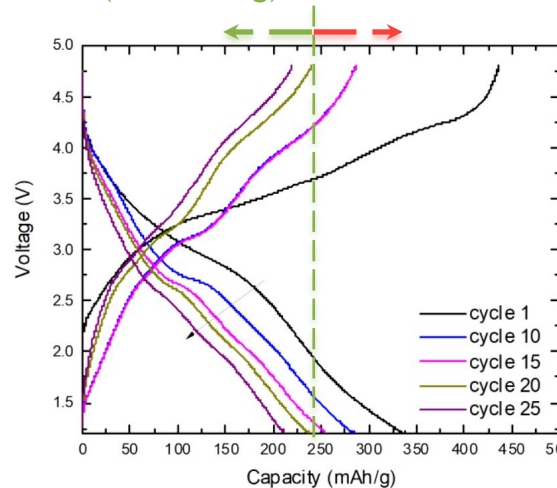
Technical Accomplishments

Electrochemical characterization of $\text{Li}_4\text{Mn}_2\text{O}_5$ – battery cycling performance

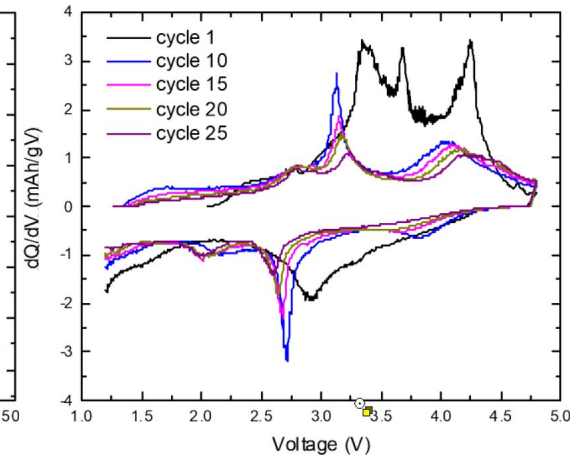
- Electrochemical properties evaluated with $\text{Li}_4\text{Mn}_2\text{O}_5$ film electrode in half-cells with Gen II electrolyte.
- A discharge capacity of ~ 350 mAh/g is obtained in the first cycle. This large capacity cannot be charge compensated only by $\text{Mn}^{3+}/\text{Mn}^{4+}$.
- dQ/dV analysis suggests that different electrochemical processes occur in the first cycle as compared to subsequent cycles.
- Gradual capacity fading and increased voltage hysteresis is observed upon battery cycling.

Theoretical capacity based on $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox (246 mAh/g)

Source of extra capacity?



Charge-discharge voltage profiles
1~25 cycles

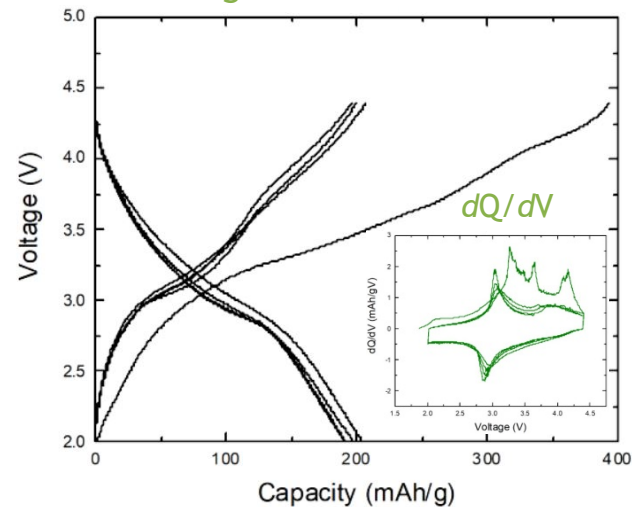


Corresponding dQ/dV profiles
1~25 cycles

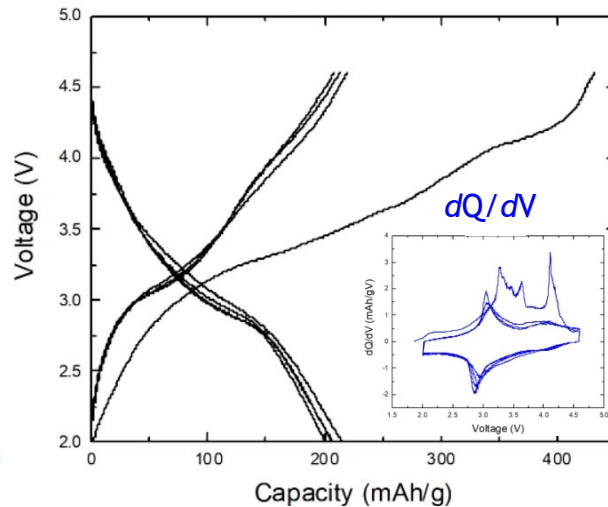
Technical Accomplishments

Electrochemical characterization of $\text{Li}_4\text{Mn}_2\text{O}_5$ – upper charge voltage varied

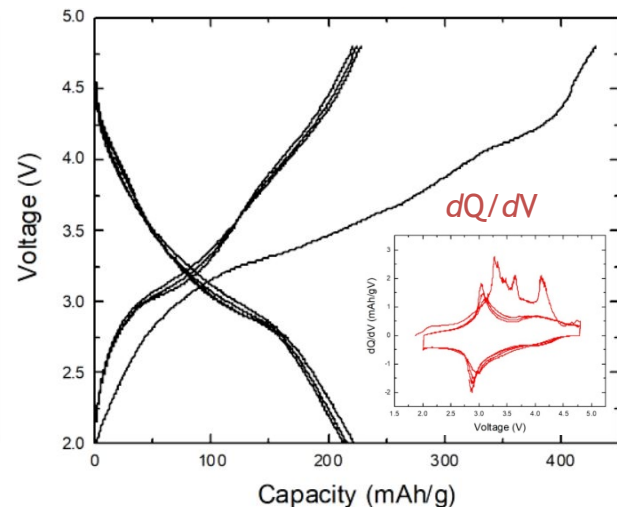
Voltage window: 4.4V-2.0V



4.6V-2.0V



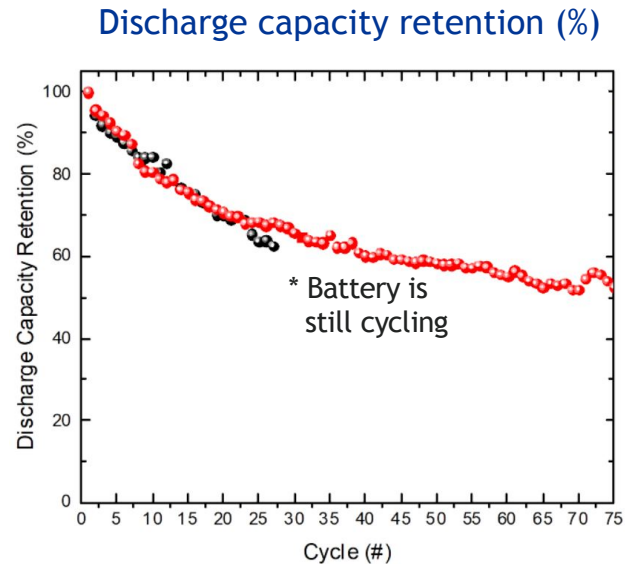
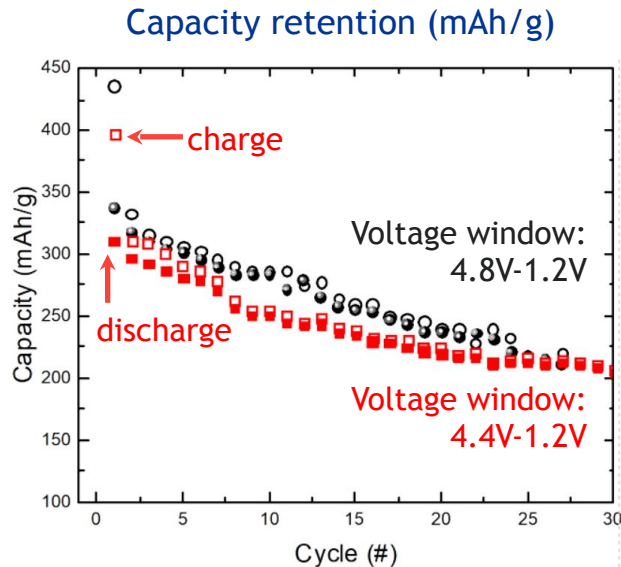
4.8V-2.0V



- Higher discharge capacity is obtained while increasing the upper charge voltage from 4.4V to 4.8V.
- Similar features observed in their corresponding dQ/dV curves suggest similar electrochemical processes.

Technical Accomplishments

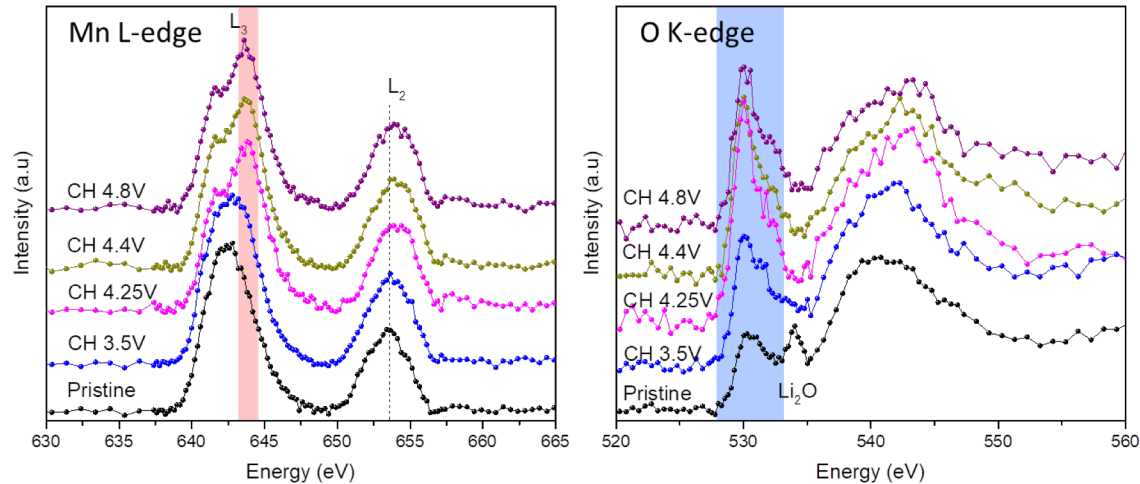
Electrochemical characterization of $\text{Li}_4\text{Mn}_2\text{O}_5$ – upper charge voltage varied



- Cycling with a lower charge voltage of 4.4V yields improved coulombic efficiency at the expense of a lower discharge capacity.

Technical Accomplishments

Ex-situ X-ray Raman Spectroscopy (XRS) characterization of $\text{Li}_4\text{Mn}_2\text{O}_5$

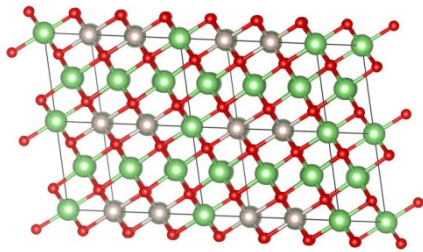


- Mn^{3+} is oxidized to Mn^{4+} by 4.25V and maintains its oxidation state on further charging to 4.8V, suggesting that the excess first-charge capacity obtained above 4.25V is not charge compensated by Mn oxidation.

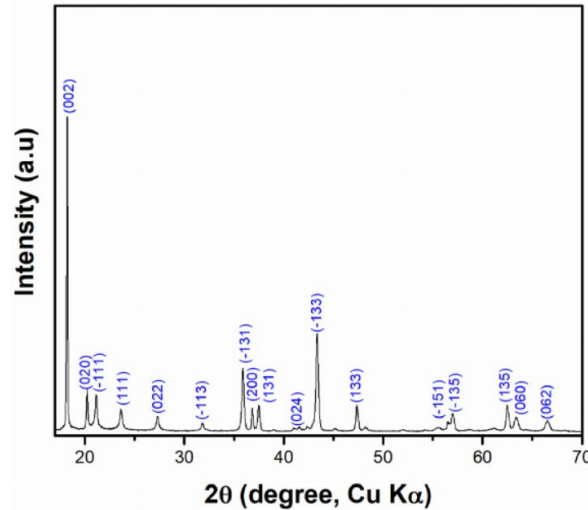
- Pristine $\text{Li}_4\text{Mn}_2\text{O}_5$ contains trace of Li_2O which is decomposed at 3.5V, contributing to a portion of the first-charge capacity.
- Changes of O K pre-edge features suggesting changes of TM-O covalency.
- Precise and complementary information about the evolution of Mn and O oxidation states requires the employment of additional synchrotron surface and bulk-sensitive techniques.

Technical Accomplishments

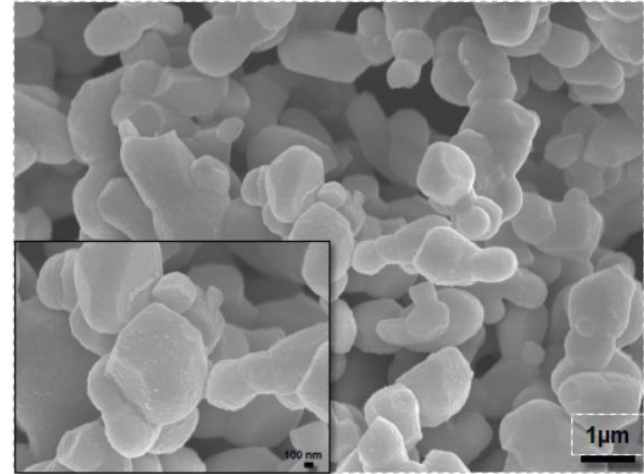
Synthesis of $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$



Layered structure



Laboratory X-ray diffraction



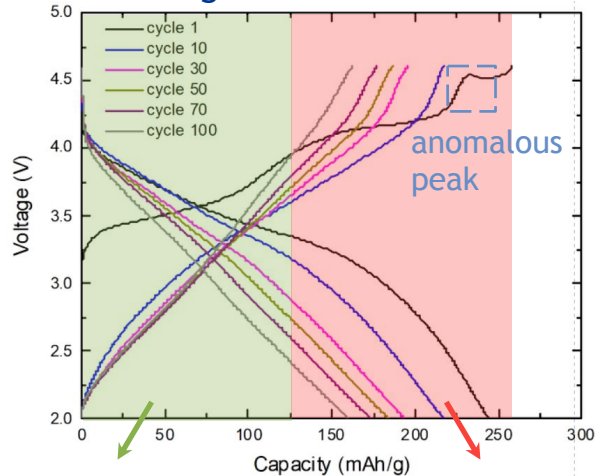
SEM image

- Layered structured $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$ with particle size ranges from 500nm to 1μm was synthesized by solid-state reactions (Sathiya *et al.*, Nat. Mater. 2013, 12, 827).

Technical Accomplishments

Electrochemical characterization of $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$

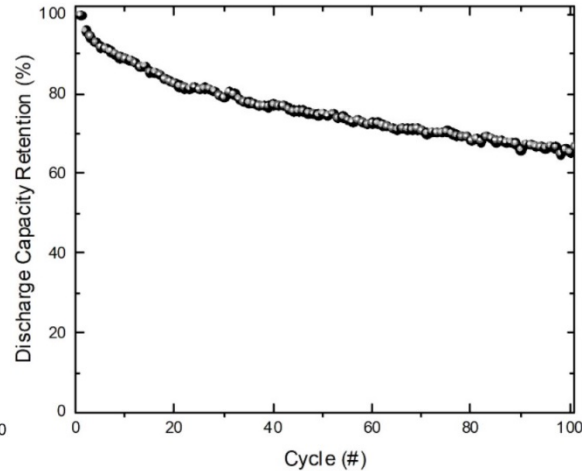
Charge-discharge voltage profiles
Voltage window: 4.8V-2.0V



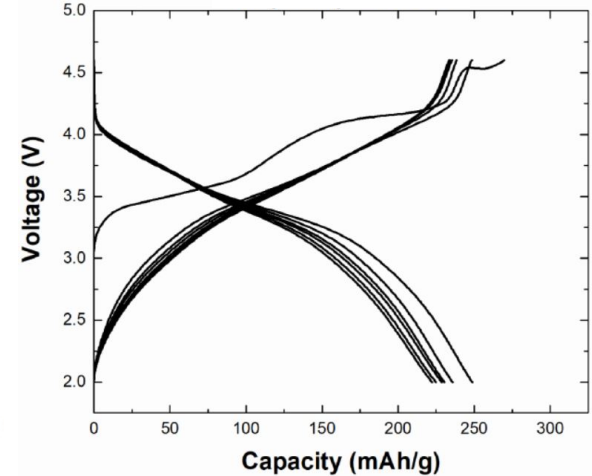
Theoretical capacity
based on $\text{Ru}^{4+}/\text{Ru}^{5+}$ redox

Extra capacity
due to O redox

Discharge capacity retention
1~100 cycles



Charge-discharge voltage profiles
Voltage window: 4.6V-2.0V

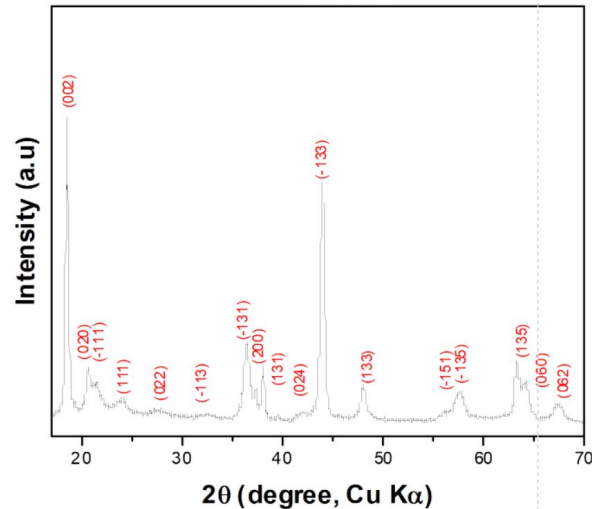


- Electrochemical properties evaluated with $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$ film electrode in half-cells.
- Typical electrochemical profiles were obtained except an anomalous oxidation peak in the first-charge at 4.6V.

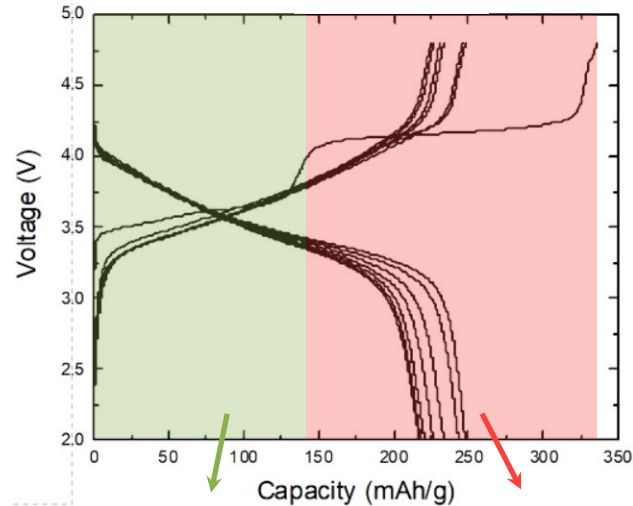
Technical Accomplishments

Synthesis and electrochemical characterization of $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$

Laboratory X-ray diffraction



Charge-discharge voltage profiles



Theoretical capacity
based on $\text{Ru}^{4+}/\text{Ru}^{5+}$ redox

Extra capacity
due to O redox

- Layered structured $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$ was synthesized by solid-state reactions (Sathiya *et al.*, Nat. Mater. 2015, 14, 230).
- The electrochemical properties are consistent with previous reports.

Response to Previous Year Reviewers' Comments

- “Approach to the technical work is solid”
- “The approach is very comprehensive but strategic”
- “To apply various techniques to characterize the materials and interfaces is exciting. Fruitful results are expected.”
- *We appreciate the positive feedback*
- “risk of spreading resources thin...consider a narrower focus to materials with true prospects of commercialization...”
- *We are narrowing the focus to manganese- and iron-based O-redox materials as requested*
- “Progress should be pushed forward aggressively”
- *Our experience applying a suite of synchrotron techniques to NMCs should allow us to make rapid progress, with the caveat that it is dependent upon availability of synchrotron facilities during the pandemic.*

Collaborations



- ❑ We work closely with beam line scientists at Stanford Synchrotron Radiation Lightsource (SSRL, Yijin Liu, Dennis Nordlund, Chenxi Wei, Thomas Kroll, Dimosthenis Sokaris) and the Advanced Light Source (ALS, Wanli Yang) on synchrotron work.
- ❑ We have collaborated in the recent past with Bosch, NA (Saravannan Kuppan, Dr. Michael Metzger) on thermal studies of NCA. However, Bosch is no longer working on batteries.
- ❑ We have collaborated recently with Virginia Tech (Dr. Feng Lin) on thermal studies on NMCs.

Remaining challenges and barriers

- ❑ Clarify the sources of excess capacities obtained with $\text{Li}_4\text{Mn}_2\text{O}_5$ (aside from those from conventional $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple): any contribution of O redox activity, irreversible O oxidation, and to what extent?
- ❑ Understand the interfacial reactivity of these materials as a function of state-of-charge, cycling history, and surface properties.
- ❑ Identify the key limitation on the first-cycle coulombic efficiency and cycling stability of these materials, how and to what extent can it be improved.
- ❑ To overcome these challenges, we rely heavily on synchrotron facilities. Beam times scheduled at SSRL and/or ALS are subject to postponement in the cases of equipment malfunction or maintenance, and unprecedented situations such as the shelter-in-place due to coronavirus.

Proposed Future Work

- ❑ Embark detailed electrochemical study on these materials to gather more information about what limits their first-cycle columbic efficiency and cycling stability (FY2020 project).
- ❑ Carry out *in situ* and *ex situ* depth-profiling characterizations on electrodes electrochemically cycled to desired state-of-charge, the results will be compared to those obtained for their chemically-delithiated counterparts, to understand their redox processes, bulk structural change, surface and interfacial evolutions (FY2020 project).
- ❑ Based on the established knowledge from FY2020, further optimize the chemical composition, and/or bulk structure, and/or surface properties of these materials, and/or the surrounding electrolyte (salt, solvent, additives), to propose effective measures to ensure their stable cycling behavior (FY2021 project).

"Any proposed future work is subject to changes based on funding levels."

Summary

- ❑ High-capacity cathode materials potentially undergoing both transition-metal and O redox were selected: one with rock-salt structure and two with layered structureA.
- ❑ Selected cathode materials have been synthesized, and characterized both electrochemically and physically.
 - A high discharge capacity of ~350 mAh/g is obtained for $\text{Li}_4\text{Mn}_2\text{O}_5$ in the first cycle. This large capacity cannot be charge compensated only by $\text{Mn}^{3+}/\text{Mn}^{4+}$, suggesting the possible participation of O redox.
 - Higher discharge capacity is obtained when cycling $\text{Li}_4\text{Mn}_2\text{O}_5$ to higher state-of-charge.
 - Excess first-charge capacity obtained above 4.25V is not charge compensated by Mn oxidation.
 - Trace of Li_2O present in the pristine $\text{Li}_4\text{Mn}_2\text{O}_5$ contributes to a portion of the first-charge capacity.
 - All the three selected materials exhibit low first-cycle columbic efficiency and gradual capacity fading during prolonged battery cycling.